ANOMALOUS MAGNETIC PROPERTIES AS A SIDE EFFEC OF LAND RECLAMATION IN THE RIA DE VIGO, NW SPAIN

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Abstract

The Ría de Vigo, on the NW coast of Spain, is a shallow marine environment with a high biological productivity and high anthropogenic pressure. The muddy sediments of the central channel of this ria incorporate annually high concentrations of organic matter that cause the onset of reductive diagenetic conditions a few centimeters below the sediment-water interface. Reductive diagenesis in the sediment dissolves the magnetic iron oxides, causing a characteristic vertical and spatial profile in the concentration of magnetic minerals. The magnetic properties of core CGVIR-13, located in an area affected by intense reductive diagenesis and heavy shipping activities, are higher and more variable that would be expected based on the natural pattern of magnetic variability in the Ría de Vigo sediments. This anomalous magnetic behavior seems to be related to the dumping of detrital material for harbor construction, and sediment resuspension and reoxygenation caused by heavy shipping activities.

Resumen

La Ría de Vigo, en la costa NO de España, es un ambiente costero con una elevada producción biológica así como una intensa presión antropogénica. Los sedimentos fangosos del canal central de la ría incorporan anualmente una elevada cantidad de materia orgánica. Como consecuencia de este aporte orgánico se establecen condiciones reductoras pocos centímetros por debajo de la interfaz agua-sedimento. Durante la diagénesis reductora los óxidos magnéticos se disuelven dando lugar a un perfil vertical y espacial de concentración magnética característico de los sedimentos de la Ría de Vigo y otras rías adyacentes. Las propiedades magnéticas del testigo CGVIR-13, localizado en una zona afectada por una intensa diagénesis reductora y una elevada actividad portuaria, son más altas y variables de lo que sería esperable según el modelo de variación magnética natural en la Ría de Vigo. Este comportamiento anómalo parece estar relacionado con la descarga de material detrítico para la construcción de rellenos portuarios, así como con la resuspensión y reoxigenación de los sedimentos debido al tráfico de grandes buques contenedores.

Introduction

Environmental magnetism has been applied to pollution studies since its early developments (e.g. Evans and Heller, 2003 and references therein). Its main advantage is its high sensitivity, the low cost and simplicity of its analyses and the fact that in most cases it is a non-destructive tool. Many studies have shown a significant relationship between dust, soil or sediment magnetic properties and the concentration and type of heavy metals or harmful dust particles. However, no known applications of environmental magnetism to detect perturbations caused by other sources of pollution, such as dumping or remobilization of sediments, exists to our knowledge.

The magnetic properties of the sediments of the Rías Baixas, in NW Spain, show a characteristic natural trend in their vertical evolution, which also varies spatially with the distance to the continent. This natural pattern is driven by early diagenesis, and is modulated by the textural, geomorphological and hydrodynamic conditions in the Ría de Vigo. This ria is the most heavily populated area in the region, and is home to a very heavy shipping industry with many large shipping vessels sailing the Ría de Vigo every day. The need to increase industrial and harbor surface led to extensive land reclamation projects. The largest of these projects took place in the Bouzas harbor in the 1950´s and again in the 1980´s and 1990´s. In this paper we present results from core CGVIR-13, located in an area adjacent to Bouzas harbor. The vertical profile of the magnetic properties of this core does not agree with the natural pattern of magnetic properties in the Ría de Vigo and other adjacent rias. This anomaly provides an excellent opportunity to study the effects of the dumping of detrital material and increase in turbulence on the magnetic properties of sediments affected by early diagenesis.

Study area

The Ría de Vigo is the southernmost of four incised fluvial valleys (Fig. 1a) that were flooded during the last sea-level transgression. Water depth ranges from 50 m at its mouth to an average 7 m in San Simon Bay, at its innermost end. Sediment distribution inside the ria is mainly controlled by wave action and limited tidal and riverine influence. Sandy sediments concentrate along its margins and near small river mouths, while fine sediments accumulate in tidal flats in the inner area and along its deep central channel.

Seasonal upwelling in the region during the summer-fall season enhances primary productivity and organic matter export to the sediment, with an estimated 9 gC m^{-2} incorporated to the Ría de Vigo sediments each year (Mohamed et al., 2011). Bacterial oxidation of this organic matter during early diagenesis rapidly consumes oxygen and causes reductive conditions that dissolve the magnetic oxides and oxyhydroxides present in the sediment (Rey et al., 2005; Mohamed et al., 2011). Reductive dissolution of minerals during early diagenesis follows a well-known sequence (Froelich et al., 1979), which is expressed in the magnetic properties of the Ría de Vigo as a three-layer zonation. The uppermost zone is dominated by magnetite, which is dissolved very rapidly in the intermediate zone. Fe sulfides are ubiquitous in the intermediate zone, also characterized by the precipitation of metastable ferrimagnetic greigite. In the lowermost zone magnetite is completely dissolved and greigite is transformed almost completely into pyrite. This vertical gradient also varies spatially as the boundaries between these zones shoal towards the internal areas. Both the vertical zonation and its spatial trend seem to be a feature characteristic of ria environments in the NW Iberian coast (Mohamed et al., 2011; Emiroglu et al., 2004; Rey et al., 2005).

Methodology

Gravity core CGVIR-13 is located in the middle sector of the Ría de Vigo (Fig. 1a). The core length is 78 cm, and water depth at this site is 42 m. The core was stored at 4ºC, split in halves along its axis, visually described, and sampled every 3 cm for magnetic analyses with plastic cylinders of standard paleomagnetic size. Mass-specific magnetic susceptibility (χ) was measured in an AGICO KLY-2 magnetic susceptibility bridge. Saturation isothermal (SIRM) and anhysteretic (ARM) remanent magnetizations were imparted and measured in a 2-G Enterprises cryogenic magnetometer with in-line alternating field (AF) demagnetizer and offline pulse magnetizer. The rest of the sample was used for grain size, total organic carbon (TOC) and total sulfur (TS) analyses. Selected magnetic samples were analyzed further under a scanning electron microscope (JEOL JSM-6700f) equipped with and energy dispersive X-ray spectroscopy probe (EDS) for determination of the composition of selected particles. To provide a framework for comparison of the magnetic properties of CGVIR-13 against the natural magnetic pattern,

we will use published data from three cores located in the external, middle, and internal sectors of the Ría de Vigo (Mohamed et al., 2011). Core CGVIR-13 is located in the same transect.

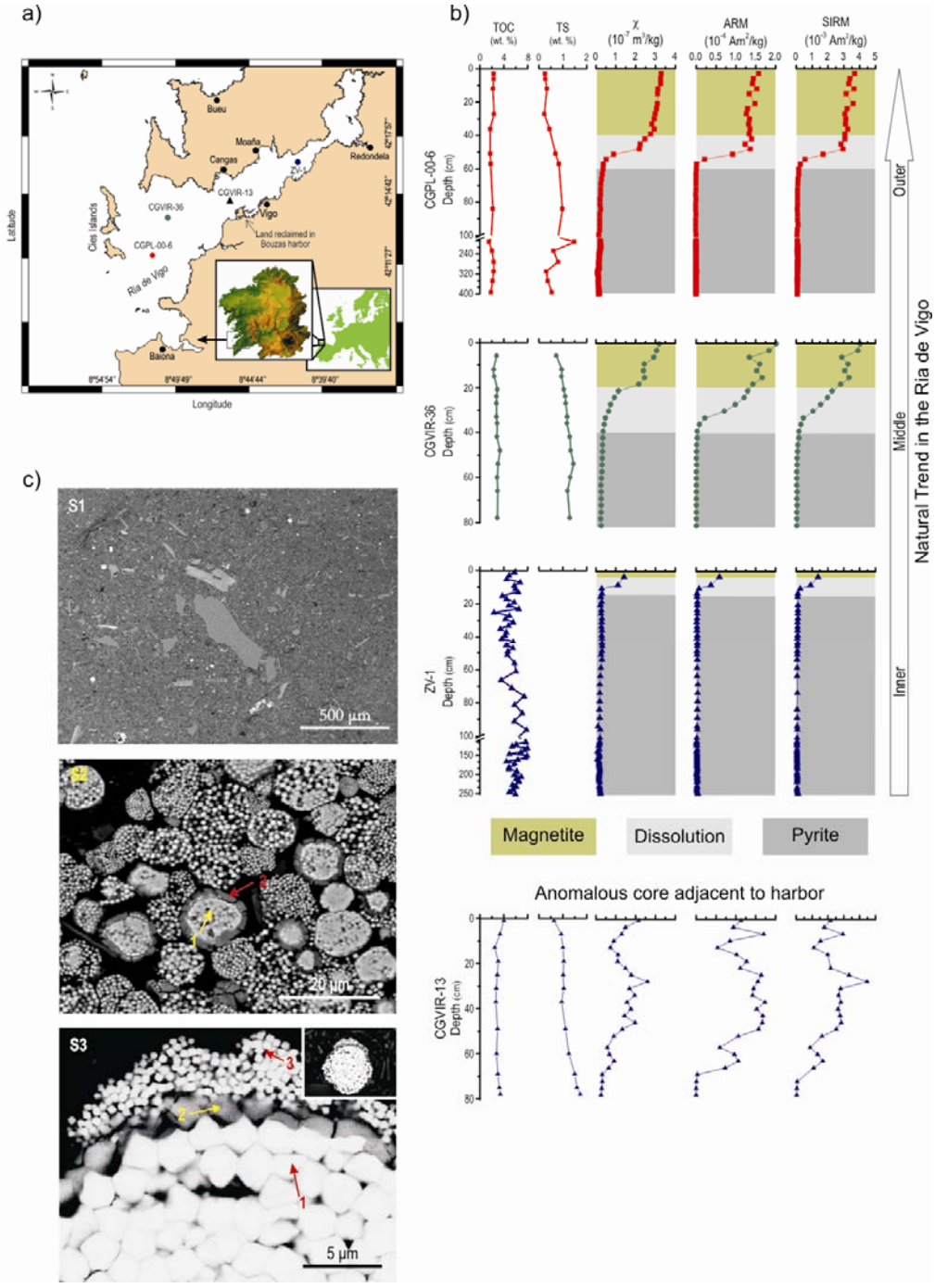

***Figure 1*. a)** Study area and location of CGVIR-13 and the cores used for comparison to the natural magnetic trend. The arrow points to the land reclaimed to build Bouzas harbor. **b)** Down core profiles of geochemical and magnetic properties discussed in the text of the three cores that define the natural magnetic trend (top) and anomalous CGVIR-13 (bottom). **c)** S1 is a general SEM view of CGVIR-13 sediments with heterometric sands in a matrix-supported fabric; S2 shows the high concentration of Fe sulfides, which in many cases (1) are covered by an oxidized edge (2); S3 is a close-up view of a framboid (1) with an oxidized edge (2) that has been subsequently overgrown by a new generation of Fe sulfides upon return of reductive conditions (3).

Results

CGVIR-13 is composed by mud, with intervals higher than 20% sand at 15-20 cm and 25-45 cm. Clay content is higher than 40% in most of the core length, and shows very little variation. TOC concentration varies between 3.0% and 4.5% in most of the core, with TS increasing from near 1% close to the core top to values near 2% at the bottom of this core.

Compared to the typical vertical profile of χ in the rest of the Ría de Vigo (Fig. 1b), core CGVIR-13 is more variable. In general terms, χ in this core decreases to a minimum at 12 cm, and increases downwards to values higher than those observed at the surface. Below 60 cm χ is similar to the bottom zone of sediments elsewhere in the Ría (Fig. 1b). SIRM and especially ARM remain high between 20 and 60 cm, with values similar to near-surface values found in other sectors of the Ría de Vigo.

A general view of CGVIR-13 sediments under the SEM shows the ubiquitous presence of Fe sulfides (Fig. 1c). Sand-sized detrital grains are common and show a matrix-supported fabric with a very heterogeneous size distribution. Fe sulfides appear mostly as framboids of variable size and brightness. Fe/S ratios determined by EDS span the range from pyrite to greigite. In many cases, a darker rim is observed on the edge of the framboids (Fig. 1c). Detailed observations and EDS analyses of this coatings show that the outer Fe sulfide cristallites are partially oxidized. In some instances a new generation of Fe sulfides grows on top of these oxidized rims (Fig. 1c).

Discussion

Core CGVIR-13 does not follow the typical spatial pattern of magnetic properties in the Galician Rías Baixas, and in particular in the Ría de Vigo (Mohamed et al., 2011). CGVIR-13 is located in high TOC muddy sediments in the middle-inner sector of the Ría de Vigo. According to the natural pattern found elsewhere in the Ría de Vigo χ should be expected to be higher in a thin upper zone, and decrease to background values a few centimeters down core.

The high concentration of magnetic sulfides observed in these sediments agrees with the natural magnetic trend. However, the oxidation of Fe sulfide cristallites in the outer rims of framboids, and the common occurrence of greigite, suggest that reductive conditions are mild and that oxidations happened subsequently to the precipitation of Fe sulfides. Furthermore, precipitation of sulfides on the oxidized rims of some framboids suggests that oxic and reductive events have alternated in these sediments.

This core is located adjacent to a landfill built to extend Bouzas harbor during the 1980's and 1990's. During these operations, thousands of tonnes of rocks and sediments were dumped in the area with no containment measures, with landfills representing 1.5% of the surface of the Ría de Vigo (Guerra et al., 2008). These construction activities increased turbulence and turbidity, promoting the export of allochthonous sediments to adjacent areas. Furthermore, up to three large car-carrier ships dock in the area almost daily. These ships may increase turbulence in the area, potentially causing resuspension of sediments by astray propeller vortexes. The observation of heterometric detrital sands floating in a matrix-supported fabric agrees with periodic sediment dumping and resuspension. Dumping of detrital material and periodic resuspension of the sediment may create recurrent oxic events that partially oxidize the Fe-sulfide framboids. Furthermore, this buffering of reductive diagenesis contributes to the preservation of greigite, a ferromagnetic mineral found in the intermediate vertical zone in other sectors of the Ría de Vigo before it rapidly transforms to pyrite as reductive diagenesis progresses. Both greigite and potential magnetic Fe oxides in the oxidized rim of the Fe sulfides explain the high and variable χ, ARM and SIRM, observed in core CGVIR-13.

Finally, the anomalous behavior of the magnetic properties of CGVIR-13 compared to the natural vertical evolution of magnetic properties in the Ría de Vigo and other adjacent rias provides an effective tool to detect subtle contamination and anthropogenic sediment resuspension in areas affected by reductive early diagenesis.

Conclusions

Core CGVIR-13 is located in a high TOC, muddy area. The down core profile of χ, SIRM and ARM, is much variable and shows higher values than would be expected based on the natural pattern of the vertical evolution of magnetic properties in the Ría de Vigo and adjacent rias (Mohamed et al., 2011). Furthermore, the occurrence of high proportions of Fe sulfide framboids is typical of sediments affected by intense reductive early diagenesis, which normally causes depletion of ferrimagnetic Fe oxides in the sediments. However, many framboids had oxidized edges, which suggests that oxic and reductive events alternate in these sediments. In addition, the positive identification of greigite in EDS analyses suggests that reductive conditions are mild and allow preservation of this mineral.

The anomalous behavior of the magnetic properties in a sediment core located near a harbor landfill provides a useful, fast and economic technique for surveying areas potentially affected by dumping and resuspension of sediments forced by anthropogenic activities.

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